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(54) [Title of the invention] Method for producing expanded vinyl-sheathed wire/cable

(57) [Abstract]
[Problem] The provision of a method for producing expanded vinyl-sheathed wire/cable having excellent electrical insulation properties, where the sheath comprises expanded vinyl chloride resin obtained using azodicarbonamide as the foaming agent.
[Overcoming means] Azodicarbonamide is mixed, in the form of an ethylene/vinyl acetate copolymer based master batch, into vinyl chloride resin composition and the resulting system is expanded to form an expanded sheath layer.

[Scope of the patent claims]

[Claim 1] Method for producing expanded vinyl-sheathed wire/cable where resin composition comprising mainly vinyl chloride resin is coated onto a conductor, and composition comprising mainly vinyl chloride resin into which foaming agent has been compounded is coated thereon to form an expanded sheath layer; characterized in that azodicarbonamide is used as said foaming agent and said azodicarbonamide is compounded, in the form of a master batch having ethylene-vinyl acetate copolymer as base resin into composition comprising mainly vinyl chloride resin.

[Claim 2] Method for producing expanded vinyl-sheathed wire/cable according to Claim 1, characterized in that the amount of azodicarbonamide compounded into said vinyl chloride resin composition is from 0.001 to 0.5% by weight.

[Claim 3] Method for producing expanded vinyl-sheathed wire/cable according to Claim 1 or 2, characterized in that the vinyl acetate content in said ethylene-vinyl acetate copolymer is from 5 to 40%.

[Detailed description of the invention]

[0001]

[Technical field of the invention] The present invention relates to a method for producing expanded vinyl-sheathed wire/cable where expanded resin composition comprising mainly vinyl chloride resin is used as a sheath.

[0002]

[Prior art] Vinyl chloride resin is excellent in terms of its electrical insulation properties, mechanical properties, flexibility and other features, and Japanese Industrial Standard JIS K 6723 stipulates that soft vinyl chloride material be used for electrical wires and cables. Generally, the resin compositions used comprise from 30 to 100 parts by weight of plasticizer, from 1 to 10 parts by weight of stabiliser and from 0 to 100 parts by weight of filler per 100 parts by weight of vinyl chloride resin, and various

additives such as lubricants and antioxidant may also be compounded if necessary.

[0003]

The soft vinyl chloride resin composition used as sheath and insulator for cables and wires is vinyl insulator vinyl sheath cable (VV) according to JIS C 3342. The cable 21 shown in Figure 1 is a flat vinyl insulator vinyl sheath cable (VVF) (that is, a flattened vinyl insulator vinyl sheath cable) and it comprises conductor 22 coated with soft vinyl chloride resin composition (insulator 23) to form insulated core wire 24, with soft vinyl chloride resin composition (sheath 25) coated thereon.

[0004]

Recently, expanded vinyl sheath cables obtained using expanded vinyl chloride resin as sheath 25 in Figure 1 have been investigated with the aim of, for example, decreasing the weight and improving the flexibility of electrical wires and cables, and keeping costs down.

[0005]

Methods for expanding vinyl chloride resins involve introducing a gas which does not react with the resin, such as nitrogen, carbon dioxide or a hydrocarbon gas such as butane or pentane, en route to the extruder, then extruding and expanding simultaneously; or expanding the resin by compounding into said resin a chemical foaming agent which generates gas on reaction or decomposition due to heat. Examples of chemical foaming agents include sodium bicarbonate, dinitroso-pentamethylenetetraamine (DPT), benzenesulphonyl hydride (BSH) and azodicarbonamide (ADCA).

[0006]

A suggested method (Japanese Unexamined Patent Application No. H5-64981) for compounding the chemical foaming agent into the vinyl chloride resin involves the use of a master batch obtained by milling a high concentration of the chemical foaming agent into the vinyl chloride resin beforehand.

[0007]

[Problem to be overcome by the invention] If the babble fraction of the sheath of the expanded vinyl-sheathed wire/cable is adjusted to around 5 to 20%, there is less of a lowering of the oil resistance and tensile strength than when an unexpanded sheath is used, and using an expanded sheath lowers costs considerably. The bubble fraction is adjusted by adjusting the type and amount of foaming agent. Azodicarbonamide is widely used as a foaming agent because it is easy to handle and produces a large amount of gas per unit mass, but if too much azodicarbonamidze is compounded, the insulation resistance increases when the wire/cable is moulded, which is disadvantageous.

[0008]

The present invention was devised in order to overcome this problem, and the aim of the present invention is the provision of a method for producing expanded vinyl-sheathed wire/cable in which the sheath comprises expanded vinyl chloride resin obtained using azodicarbonamide as the foaming agent, and which can result in excellent insulating performance.

[0009]

[Means of overcoming the problem] As a result of diligent research into overcoming the abovementioned problem, the present inventors perfected the present invention upon ascertaining that foaming agent decomposition products generated during the moulding of the sheath migrate into the insulator and have an adverse affect on the electrical insulation performance of said insulator. Specifically, the present invention provides (1) a method for producing expanded vinyl-sheathed wire/cable where resin composition comprising mainly vinyl chloride resin is coated onto a conductor, and composition comprising mainly vinyl chloride resin into which foaming agent has been compounded is coated thereon to form an expanded sheath layer; where azodicarbonamide is used as said foaming agent and said azodicarbonamide is compounded, in the form of a master

batch having ethylene-vinyl acetate copolymer as base resin, into composition comprising mainly vinyl chloride resin; (2) the method for producing expanded vinyl-sheathed wire/cable disclosed in (1), where the amount of azodicarbonamide compounded into said vinyl chloride resin composition is from 0.001 to 0.5% by weight; and (3) the method for producing expanded vinyl-sheathed wire/cable disclosed in (1) or (2), where the vinyl acetate content in said ethylene-vinyl acetate copolymer is from 5 to 40%.

[0010]

[Mode of the invention] The sheath of the inventive expanded vinyl-sheathed wire/cable is expanded soft vinyl chloride resin composition for wires and cables, as stipulated by JIS K 6723. The azodicarbonamide foaming agent is used compounded into vinyl chloride resin composition in the form of a master batch comprising ethylene-vinyl acetate copolymer as base resin. The proportion of azodicarbonamide compounded is suitably from 1 to 50% by weight of the master batch. Other additives such as antioxidants and colorants may also be compounded into the master batch. Furthermore, the proportion of azodicarbonamide compounded into the soft vinyl chloride resin composition should be adjusted depending on the bubble fraction of the sheath, and is suitably from 0.001 to 0.5% by weight. In the inventive production method, the azodicarbonamide is used in the form of a master batch obtained by milling said azodicarbonamide into ethylene-vinyl acetate copolymer, and so it is possible to increase the foaming efficacy while keeping the amount of azodicarbonamide used to a very small amount, which in turn can greatly decrease the adverse effect of azodicarbonamide decomposition products on the electrical properties of the insulator, thereby allowing the efficient production of expanded vinyl-sheathed wire/cable of excellent electrical insulation properties.

[0011]

The inventive production method overcomes the problem that arises when azodicarbonamide is used as the foaming agent by conventional methods, while achieving the same efficacy as when p,p'-oxybisbenzenesulphonyl hydride (OBSH) or the like is used as foaming agent.

[0012]

The ethylene-vinyl acetate copolymer used as the base resin for the master batch preferably has a vinyl acetate content of from 5 to 40%, in view of fluidity and miscibility with vinyl chloride resin.

[0013]

Commercially available ethylene-vinyl acetate copolymer can be used, such as Ultrasen 537, Ultrasen 540, Ultrasen 541, Ultrasen 625, Ultrasen 633 and Ultrasen 681, manufactured by Tosoh (K.K.), Evaflex P-1207 and P-1907, manufactured by Mitsui DuPont Chemicals (K.K.), and Jayrex EVA DL19-8 and Jayrex EVA DL12-5, manufactured by Nippon Polyolefin (K.K.).

[0014]

The master batch must be sufficiently dispersed in the vinyl chloride resin composition. The decomposition temperature of azodicarbonamide is around 200°C, but when it is compounded in vinyl chloride resin composition, lead and zinc compounds act as catalyst and the composition temperature is lower. For example, when tribasic lead sulphate is compounded as stabiliser the decomposition temperature of the azodicarbonamide decreases to 160°C, and so sufficient decomposition certainly proceeds in the vinyl chloride resin composition processing temperature range of from 180 to 200°C. However, if there is insufficient dispersion the azodicarbonamide cannot come into contact with the catalysts and so foaming becomes uneven and the bubble size becomes non uniform. The master batch must therefore be thoroughly dispersed.

[0015]

Soft vinyl chloride resin compositions which can be used in the present invention usually comprise from 30

to 100 parts by weight of plasticizer, from 1 to 10 parts by weight of stabiliser and from 0 to 100 parts by weight of filler per 100 parts by weight of vinyl chloride resin, and improving agents, and various additives such as lubricants, antioxidants and photostabilizers, may also be compounded if necessary.

[0016]

There are no particular limitations regarding the plasticizer used for vinyl chloride resin, and examples include phthalic acid-based, trimellitic acid-based, adipic acid-based and polyester-based plasticizers.

[0017]

Examples of the stabilisers are lead stabilisers and Ca/Zn-based stabilisers, tin-based stabilisers, phosphite-based stabilisers and epoxy compounds. Examples of the lead stabilisers are tribasic lead sulphate, tribasic lead maleate, dibasic lead stearate, dibasic lead phthalate, white lead, dibasic lead phosphite and basic lead sulphite. Examples of the Ca/Zn-based stabilisers are calcium stearate, calcium ricinoleate, calcium laurate, zinc stearate, zinc ricinoleate and zinc laurate. Also, perchloric acid-type hydrotalcite or commercially available hydrotalcite such as Alkamizer 1 to 5 manufactured by Kyowa Kagaku Kogyo (K.K.) may be added as stabiliser. The tin-based stabilisers include organotin mercaptide, organotin maleate and organotin carboxylate.

[0018]

The filler is an extender commonly used for vinyl chloride resin compositions, such as calcium carbonate, kaolin clay or talc. Heavy calcium carbonate obtained by pulverising natural stone such as limestone, and sedimented calcium carbonate obtained by chemical methods are examples of calcium carbonate which can be used, and products obtained by surface-treating these may also be used.

[0019]

[Working examples] The present invention is described below based on working examples. The soft vinyl

chloride resin compound material for insulators shown in Table 1, and the soft vinyl chloride resin compound material for sheaths shown in Table 2, were independently milled using rollers set at 160°C, and moulded into 2 mm thick sheets, then these were pelleted using a pelletizer to yield 2 mm square pellets of soft vinyl chloride resin compound.

[0020]

[Table 1]

Soft polyvinyl chloride compound for insulator

		Amount compounded (parts by weight)	Tradename etc.
Polyvinyl chloride		100	Shin Dai'ichi Envi (K.K.) ZEST1300
Plasticiser	DOP	50	Chisso (K.K.)
Filler	Calcium carbonate Clay	15 15	Takehara Kagaku Kogyo (K.K.) Sunlite SL-1500 ENGELHARD SATINTONE SP-33
Stabiliser	Tribasic lead sulphate Dibasic lead stearate	3 1	Mizusawa Kagaku Kogyo (K.K.) Stavinex TC Mizusawa Kagaku Kogyo (K.K.) Stavinex C18

[0021]

[Table 2]

Soft polyvinyl chloride compound for sheath

		Amount compounded (parts by weight)	Tradename
Polyvinyl chloride		100	Shin Dai'ichi Envi (K.K.) ZEST1300
Plasticiser	DOP	50	Chisso (K.K.)
Filler	Calcium carbonate	15	Takehara Kagaku Kogyo (K.K.) Sunlite SL-1500
Stabiliser	Tribasic lead sulphate Dibasic lead stearate	3 1	Mizusawa Kagaku Kogyo (K.K.) Stavinex TC Mizusawa Kagaku Kogyo (K.K.) Stavinex C18

[0022] Four types of master batch pellets of the compositions shown in Table 3 were also prepared, using soft vinyl chloride compound by the same method. It should be noted that the roller temperature during the milling of the resin was 100°C for master batches 1 to 3 and 160°C for master batch 4.

[0023]

[Table 3]

Foaming agent master batch

			Amount compounded	Tradename
Master batch 1	Ethylene-vinyl acetate copolymer (vinyl acetate content 10%)		80	Tosoh (K.K.) Ultrasen 541
	Azodicarbonamide		20	Daimichi Seika (K.K.) Daiblow AC2040L
Master batch 2	Ethylene-vinyl acetate copolymer (vinyl acetate content 5%)		80	Nippon polyolefin (K.K.) BM 17-50
	Azodicarbonamide		20	Diaimichi Seika (K.K.) Daiblow AC2040L
Master batch 3	Ethylene-vinyl acetate copolymer (vinyl acetate content 42%)		80	Tosoh (K.K.) Ultrasen 760
	Azodicarbonamide		20	Daimichi Seika (K.K.) Daiblow AC2040L
Master batch 4 (conventional master batch)	Polyvinyl chloride		100	Shin Dai'ichi Envi (K.K.) ZEST1000
	plasticizer	DOP	55	Chisso (K.K.)
	stabiliser	Tribasic lead sulphate	3	Mizusawa (K.K.) Stavinex TC
		Dibasic lead stearate	1	Mizusawa (K.K.) Stavinex C18
	foaming agent	azodicarbon-amide	20	Daimichi Seika (K.K.) Daiblow AC2040L

[0024] (Working Example 1)

The soft vinyl chloride resin compound for the insulator was melt-milled using an extruder (L/D 24, screw diameter 30 mm) and extrusion coated to a thickness of 0.8 mm on to 1 mm diameter copper wire to yield an insulated wire core. The soft vinyl chloride resin compound for the sheath, and master batch 1, were melt-milled in the proportions shown in Table 4 using an extruder (L/D 24, screw diameter 30 mm) to form a resin composition, and said resin composition was extrusion coated to a thickness of 1.5 mm onto the abovementioned insulated wire core and expanded to form an expanded sheath layer, thereby yielding the expanded vinyl-sheathed wire of Working Example 1.

[0025]

(Working Examples 2 to 5 and Comparative Examples 1 and 2)

Expanded vinyl-sheathed wire was prepared as in Working Example 1, except that the types and amounts of master batch shown in Table 4 were used.

[0026]

The resulting expanded vinyl-sheathed wires were taken and, as a rule, the bubble fraction of the sheath layer and the insulation resistance were measured and the appearance of the expanded cells was observed, according to the methods described below. The results are also shown in Table 4.

[0027] Bubble fraction of the sheath layer: The density of the sheath layer was measured before and after expansion, and the bubble fraction was calculated using the following equation

Bubble fraction (%) = (density before expansion - density after expansion) × 100/density before expansion

[0028]

Insulation resistance: This was measured according to the method stipulated in JIS C 3005 (1993) 9.1 (1) (insulation resistance at 20°C).

[0029]

Expanded cell appearance: The wire was cut perpendicular to its lengthwise direction and the sheath layer cross section was examined visually and given one of 3 appraisal grades, O Δ or ×, where O indicates fine uniformity.

[0030]

[Table 4]

			Working example					Comparative example	
			1	2	3	4	5	1	2
Polyvinyl chloride composition (part by weight)	polyvinyl chloride compound for sheath		99.5	99.0	97.5	99.0	99.0	99.0	95.0
	foaming agent master batch	master batch 1	0.5	1.0	2.5				
		master batch 2				1.0			
		master batch 3					1.0		
		master batch 4						1.0	5.0
Azodicarboxamide content in the polyvinyl chloride resin (%)			0.1	0.2	0.5	0.2	0.2	0.2	1.0
Appraisal/ measurement	bubble fraction (%)		9.8	15.8	40.3	10.2	9.5	2.4	15.3
	insulation resistance (MΩ . km)		250	180	95	195	200	200	45
	expanded cell appearance		O	O	O	O	O	Δ	×

[0031] The expanded vinyl-sheathed wires of Working Examples 1 to 5 were such that the sheath layers had a high bubble fraction and a good insulation resistance and expanded cell appearance, and said wires had excellent electrical properties. Specifically, in Working Example 2 (where the master batch was prepared using ethylene-vinyl acetate copolymer having a vinyl acetate content of 10%) exhibited a higher bubble fraction than Working Examples 4 and 5 (having the same amount of diazodicarbonamide added). Moreover, although Comparative Example 1 (obtained using master batch having conventional vinyl chloride resin as the base resin) had the same amount of azodicarbonamide added as Working Examples 2, 4 and 5, its bubble fraction was much lower. Comparative Example 2 (obtained by increasing the amount of azodicarbonamide added to 5%) resulted in a sheath layer of the same bubble fraction as achieved in Working Example 2, but the insulation resistance was considerably lower.

[0032]

[Advantages of the invention]

The inventive production method allows the production of expanded vinyl-sheathed wire/cable having excellent insulation properties, where the sheath comprises expanded vinyl chloride resin obtained using azodicarbonamide as the foaming agent.

[Brief description of the Figure]

[Figure 1]

A diagram showing the construction of a vinyl insulator vinyl sheath cable.

[Legend]

21 cable

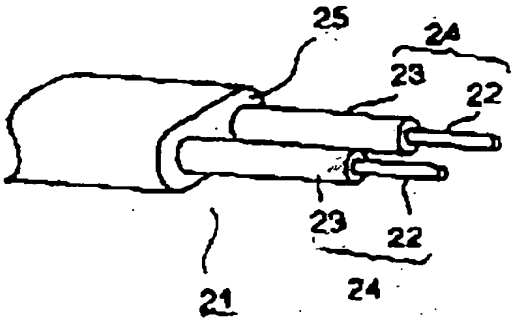
22 conductor

23 insulator

24 insulated wire core

25 sheath

[Figure 1]



Translator's Report/Comments

In translating the above text we have noted the following apparent errors/unclear passages which we have corrected or amended:

Page/para/line*	Comment
	Japanese proper nouns can have several possible readings; common readings have been chosen throughout. We have been unable to confirm the official English spellings of tradenames etc. given phonetically in the original. For example, the term "Ultrasen"has been derived from the term given phonetically as *urutorasen*, but the English spelling could not be confirmed.

* This identification refers to the source text. Please note that the first paragraph is taken to be, where relevant, the end portion of a paragraph starting on the preceding page. Where the paragraph is stated, the line number relates to the particular paragraph. Where no paragraph is stated, the line number refers to the page margin line number.